

AD-A084 128

UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT 0--ETC F/G 7/4
QUENCHING OF EMISSION AND OF PHOTOCHEMISTRY OF PENTACARBONYL-4-
MAY 80 A J LEES, A W ADAMSON N00014-76-C-0548

UNCLASSIFIED

TR-9

NL

1 OF 1
AD
A084 128

26

END
DATE
FORMED
6-80
DTIC

ADA 084128

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO. AD-A084128	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Quenching of Emission and of Photochemistry of Pentacarbonyl-4-cyanopyridinotungsten(0)		5. TYPE OF REPORT / PERIOD COVERED 9 Technical Report 1980
7. AUTHOR(s) 10 Alistair J. / Lees Arthur W. / Adamson		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Department of Chemistry Los Angeles, California 90007		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-76-C-0548
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 472) Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-609
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 15 14 TR-9		12. REPORT DATE May 80
		13. NUMBER OF PAGES 10
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		LEVEL II DTIC ELECTE MAY 13 1980 S D E
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photochemistry Tungsten carbonyls Pentacarbonyl-4-cyanopyridino- Emission Group VI carbonyls tungsten(0) Quenching 4-cyanopyridine		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See manuscript.		

DD FORM 1473 1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014 6501

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

80 5 12 043

DOC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0548

Task No. NR 051-609

TECHNICAL REPORT NO. 9

Quenching of Emission and of Photochemistry of
Pentacarbonyl-4-cyanopyridinotungsten(0)

by

Alistair J. Lees and Arthur W. Adamson

Prepared for Publication

in the

Journal of the American Chemical Society

University of Southern California
Department of Chemistry
Los Angeles, California 90007

May 6, 1980

Accession For	
NTIS GML&I	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Serials Codes	
Dist	A. all and/or special
A	

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited.

Quenching of Emission and of Photochemistry of
Pentacarbonyl-4-cyanopyridinetungsten(0)

Alistair J. Lees and Arthur W. Adamson

Department of Chemistry

University of Southern California

Los Angeles, California 90007

Abstract

The complex $W(CO)_5L$, $L = 4$ cyanopyridine, is found to emit in room temperature methylcyclohexane solution. The emission is centered around 630 nm and is 105 ± 10 nsec in lifetime, τ , at 25 °C. Added 0.1 M ethanol does not change the characteristics, and in this medium $1/\tau = 2.61 \times 10^8 \exp(-1960/RT)$. The emission is quenched by anthracene, as is also the photosubstitution reaction whereby L is replaced by ethanol ($\phi = 0.028 \pm 10\%$ at room temperature), Stern-Volmer plots of (τ^0/τ) and of (ϕ^0/ϕ) vs. quencher concentration are linear, the common slope giving a bimolecular quenching rate constant of $3.7 \times 10^9 M^{-1} sec^{-1}$. The charge transfer (CT) emitting state is clearly implicated in the photochemistry; between the emission spectrum and the anthracene triplet state energy, the energy of the CT state is bracketed as between 14.7 and 20 kK.

Quenching of Emission and of Photochemistry of
Pentacarbonyl-4-cyanopyridinetungsten(0).

Sir:

Several complexes of the general formula $W(CO)_5L$, where L is a n-donor, have been found to luminesce at 77K either as the pure solid or in rigid glasses.^{1,2} The emission has been assigned to either a $^3E \rightarrow ^1A_1$ ligand field (LF) transition or a $W \rightarrow L$ charge transfer (CT) transition, depending on the nature of L. As L becomes more electron-withdrawing, the CT state lowers in energy, and for various 4-substituted pyridines as L, has been inferred to be the lowest lying state.³ $W(CO)_5L$ complexes have not been thought to luminesce in room temperature solution, presumably because of rapid ligand dissociation and non-radiative relaxation to ground state.^{2,4} We report here what appears to be the first observation of emission from a $W(CO)_5L$ complex in room temperature solution. The finding makes possible quenching studies, and results are reported for anthracene as quencher.

$W(CO)_5(4\text{-cyanopyridine})$ was prepared via the tetrahydrofuran complex, $W(CO)_5(THF)$, according to a literature procedure.^{3,5} Purification was achieved by chromatography on alumina, followed by recrystallization from toluene/iso-octane solution. Anthracene was recrystallized from benzene prior to use. The solvent methylcyclohexane was purified by distillation, to remove trace emitting impurities. Laser pulse excitation was at 353 nm or 530 nm, using a 20 nsec pulse from a Nd glass laser.⁶ Conventional photolyses were carried out with light from an interference filtered Hg lamp, and quantum yields were determined by means of Reineckate actinometry.⁷

Either 353 nm or 530 nm excitation of $W(CO)_5(4\text{-cyanopyridine})$ (5×10^{-5} to $1 \times 10^{-4} M$) in argon-flushed⁸ methylcyclohexane produced a relatively weak emission (comparable in intensity to that found for various Cr(III) amines in room temperature solution⁹). The decay time, τ , is 105 ± 10 nsec at 25 °C, and the emission is in the 600-700 nm region with an uncorrected peak intensity at about 630 nm (reported values in EPA at 77 K are 33 μ sec and 602 nm³). The emission temperature dependence was determined both in the above solvent and with added 0.1 M ethanol (which had no detectable effect). The data are shown in Figure 1, the least squares line giving $1/\tau = 2.61 \times 10^8 \exp(-1960/RT)$; the apparent activation energy is thus small, and may relate to that of solvent viscosity. It might be noted that we see weak emission from such complexes as $W(CO)_6$ and $W(CO)_5(C_2H_5OH)$, but of lifetime less than 20 nsec, so that quenching studies were not attempted.

In the absence of some entering ligand, the photochemistry is complex. Photodissociation of the 4-cyanopyridine or similar ligands has been found to be the most efficient process for our excitation wavelength region,^{3,10} and binuclear species such as $W_2(CO)_{11}$ or $W_2(CO)_{10}L$ may be formed.¹¹ Also, for example, evidence has recently been reported for the appearance of $Cr_2(CO)_{11}$ on flash photolysis of $Cr(CO)_6$ in perfluorocarbon solvents.¹² We observed an early loss of isobestic points on photolysis of $W(CO)_5(4\text{-cyanopyridine})$ in methylcyclohexane, evidently due to secondary reactions to form such binuclear products. However, in the presence of excess entering ligand, in this case 0.1 M ethanol, the photosubstitution reaction to form $W(CO)_5(C_2H_5OH)$ appears to be uncomplicated by side or subsequent reactions. The spectral sequence on 520 nm irradiation is shown in Figure 2; there is a clean progression to near zero terminal absorbance in the 450 nm to 500 nm region. The quantum yield, ϕ , is $0.028 \pm 10\%$; such a low value is

consistent with results reported for substituted pyridine ligands of this type,³ and is apparently characteristic when the CT state lies below the LF state.

Quenching both of the photochemistry and of the luminescence is observed using anthracene. A Stern-Volmer type plot of ϕ^0/ϕ and τ^0/τ , where superscript zero denotes absence of quencher, is linear against anthracene concentration, as shown in Figure 3. The slope yields a common bimolecular quenching rate constant of $3.7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. This value is at about the diffusion limit.

Our results strongly indicate that the emitting state of $\text{W(CO)}_5(4\text{-cyanopyridine})$ is directly implicated in the photochemistry. Presumably, reaction occurs from this state, although back intersystem crossing to a reactive LF state is an alternative possibility, especially if ϕ turns out to be strongly temperature dependent. We can put limits on the energy of the emitting state. From the emission spectrum, it appears to be not more than 20 kK, and, assuming that quenching is by energy transfer, the lower limit is that of triplet state anthracene, or 14.7 kK.¹³ Investigations are in progress to locate this energy more precisely and also to verify that energy transfer is indeed the quenching mechanism.

Quenching of emission and of photochemistry has been observed for various Cr(III) amines,¹⁴ and, recently for $\text{Rh(NH}_3)_5\text{Cl}$ ¹⁵ and $\text{Rh(NH}_3)_5\text{Br}$.¹⁶ Emission and emission quenching has been reported for Rhenium tricarbonyl complexes.¹⁷ The present case appears to be the first one involving a Group VI carbonyl complex.

Acknowledgement

This investigation was supported in part by a grant from the U.S.
Office of Naval Research.

Alistair J. Lees and Arthur W. Adamson
Department of Chemistry
University of Southern California
Los Angeles, California 90007

References and Notes

- (1) a. Wrighton, M.; Hammond, G.S.; Gray, H.B. J. Am. Chem. Soc. 1971, 93, 4336; b. Inorg. Chem. 1972, 11, 3122.
- (2) Wrighton, M. Chem. Rev. 1974, 74, 401.
- (3) Wrighton, M.S.; Abrahamson, H.B.; Morse, D.L. J. Am. Chem. Soc. 1976, 98, 4105.
- (4) Koerner von Gustorf, E; Grevels, F. W. Fortschr. Chem. Forsch. 1969, 13, 366.
- (5) Strohmeier, W. Angew. Chem. Internat. Ed. 1964, 3, 730.
- (6) See Gutierrez, A.R.; Adamson, A.W. J. Phys. Chem. 1978, 82, 902.
- (7) Wegner, E.E.; Adamson, A. W. J. Am. Chem. Soc. 1966, 88, 394.
- (8) Argon purging was precautionary - lack of it did not affect the lifetime.
- (9) Walters, R. T.; Adamson, A. W. Acta Chem. Scand. A 1979, 33, 53.
- (10) a. Dahlgren, R. M.; Zink, J. I. Inorg. Chem. 1977, 16, 3154; b. J. Am. Chem. Soc. 1979, 101, 1448.
- (11) Graham, M. A.; Poliakoff, M.; Turner, J. J. J. Chem. Soc. A 1971, 2939.
- (12) Bonneau, R.; Kelly, J. M. J. Am. Chem. Soc. 1980, 102, 1220.
- (13) Birks, J. B. "Photophysics at Aromatic Molecules," Wiley-Interscience, New York, 1970, p. 182.
- (14) See Zinato, E. "Concepts of Inorganic Photochemistry," Adamson, A. W.; Fleischauer, P.D. eds., Wiley-Interscience, New York, 1975, p. 143.
- (15) Adamson, A. W.; Fukuda, R.C.; Larson, M.; Macke, H.; Paux, J. P. Inorg. Chim. Acta 1980, 44, L13.
- (16) Larson, M.; Adamson, A. W.; Rumfeldt, R. C. J. Am. Chem. Soc., submitted.
- (17) Wrighton, M.; Morse, D. L. J. Am. Chem. Soc. 1974, 96, 998.

Legends for the Figures

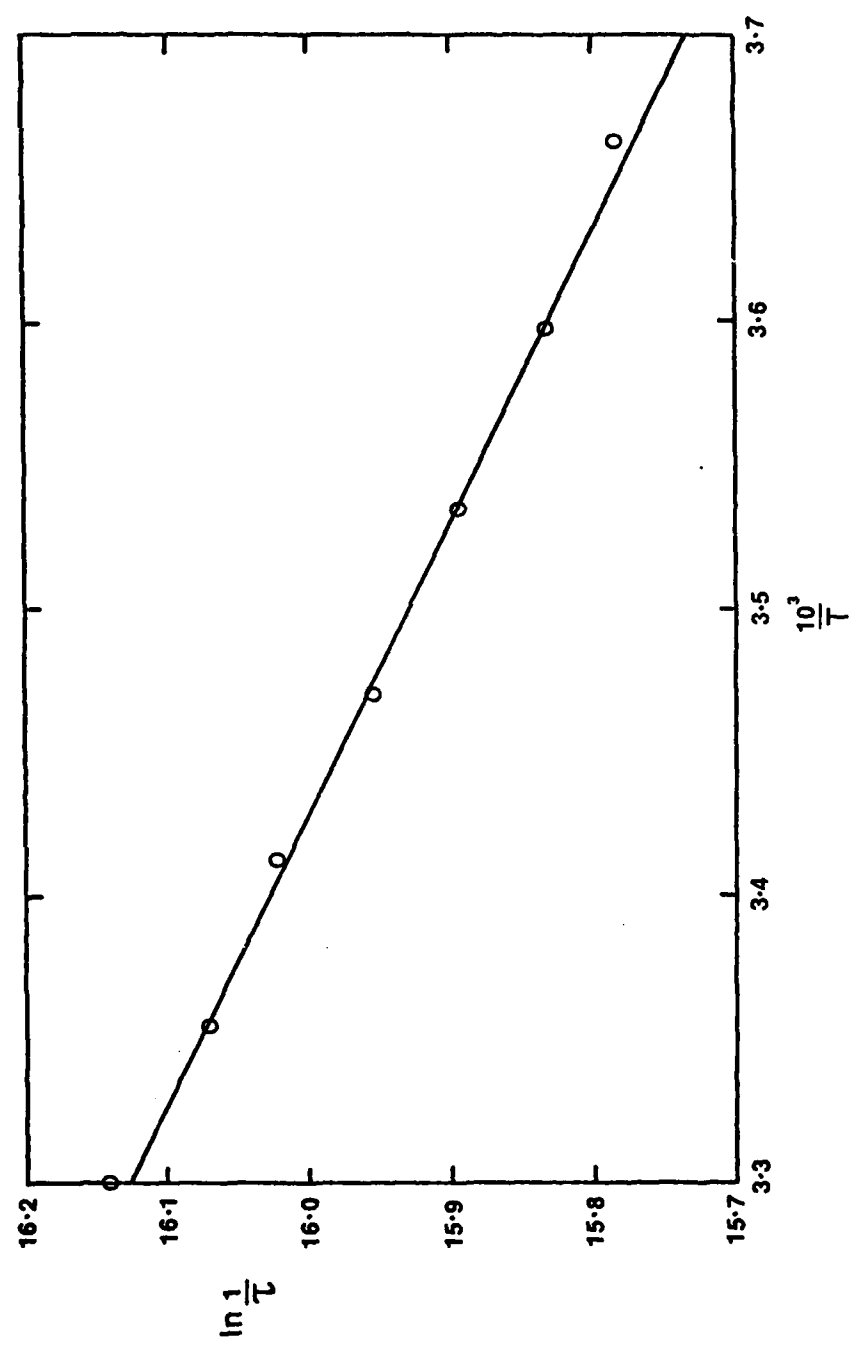
Figure 1. Temperature dependence of emission from $W(CO)_5(4\text{-cyanopyridine})$ in argon purged methylcyclohexane containing 0.1 M ethanol. Excitation at 530 nm detection at 650 nm.

Figure 2. Photolysis of $W(CO)_5(4\text{-cyanopyridine})$ at room temperature in methylcyclohexane containing 0.1 M ethanol. Curve 1, initial spectrum. Curves 2-7, irradiation at 520 nm for equal time intervals.

Figure 3. Quenching of $W(CO)_5(4\text{-cyanopyridine})$ processes at room temperature by anthracene in methylcyclohexane containing 0.1 M ethanol. $0, \tau^0/\tau, X, \phi^0/\phi$.

A. J. Lees, A. W. R. Jones

Fig 1



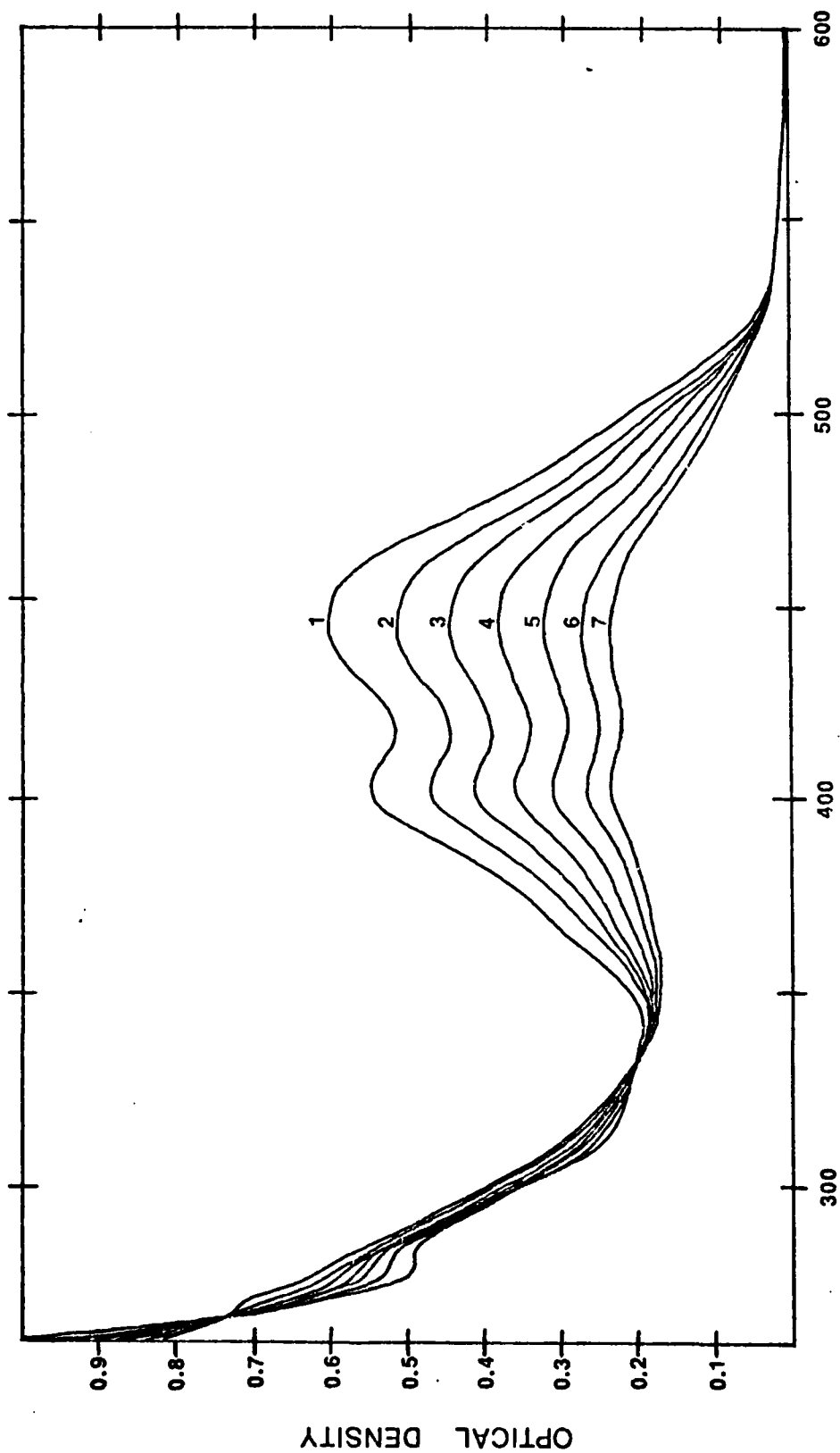


Fig 2

PLASMA R 10 ALUMINUM

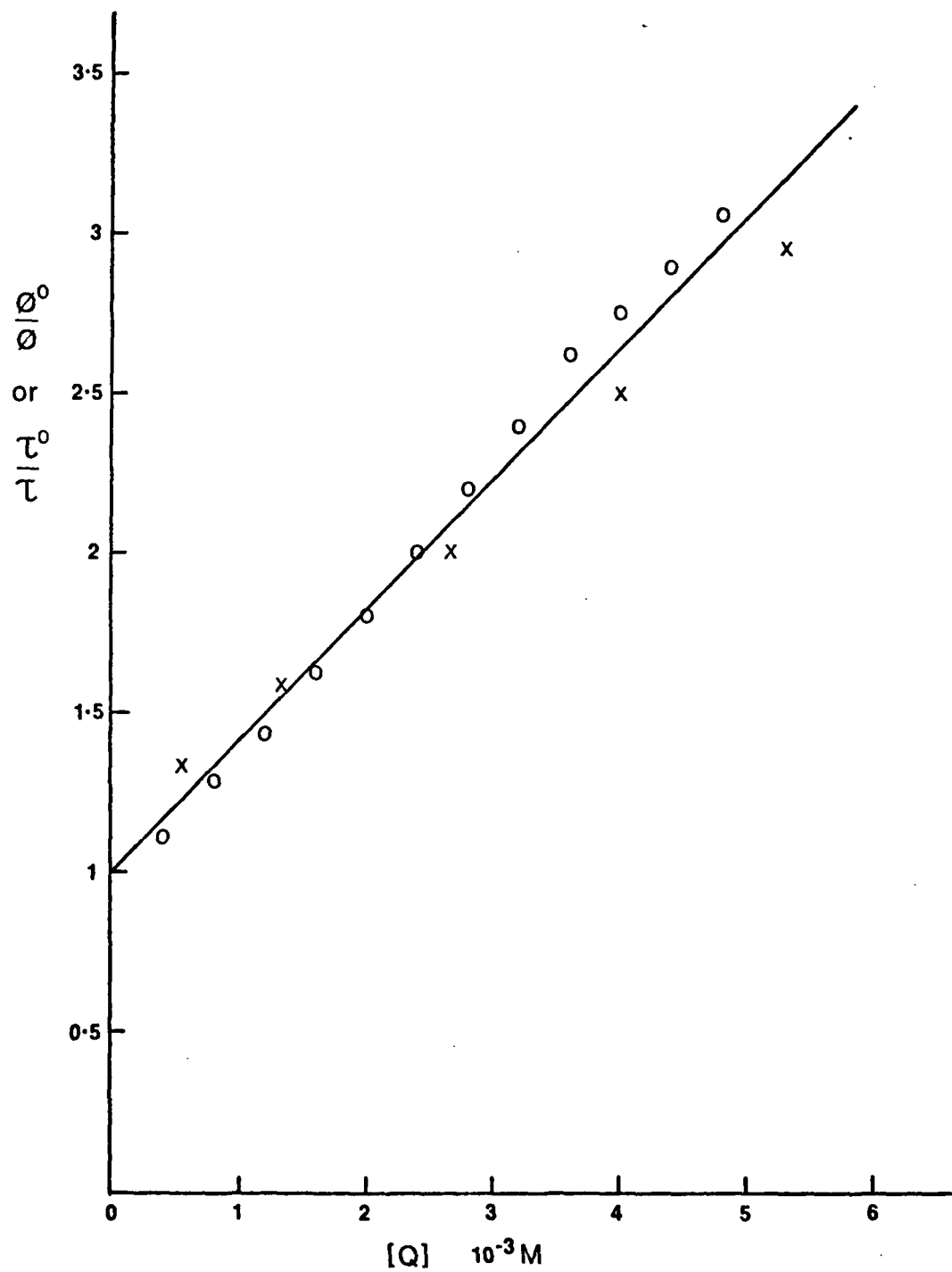


Fig 3

P. J. L. ... H. B. Hansen

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1	Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08805	1
Dr. M. W. Windsor Department of Chemistry Washington State University Pullman, Washington 99163	1	Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1	Dr. B. Schechtman IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. J. R. MacDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1		
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1		
Dr. E. M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah	1		
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1		
Dr. M. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		